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The Rate of Hydrolysis of Some Organophosphates Chemical Studies on Organophosphorus Insecticides IV

AUTHOR(S):

SATŌ, Rokurō; KUBO, Hiroshi

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ings, especially it was remarkable in *P. picea*. The amount of consumption of some cereals in *P. picea* was slightly increased by adding a small quantity of sugar.

It is an interesting feature that roaches were very fond of casein. The other practical tests with roach control showed that some sweetenings such as sugar or molasses increased the effectiveness of certain bait formulations containing a given amount of lindane or chlordane.

Discussion

Since the roach has developed resistance to some insecticides, new scientific method to control these insects must be developed. Poison bait application may be one of them which serves this purpose, since a bait guides and detains an insect to a place existing some deposits of insecticide.

It has been long-established that a number of vegetable materials such as wheat bran, rice-bran, maize meal, and others are helpful for the preparation of poison baits to control certain agricultural pests⁵⁾. The fact that the effectiveness of certain insecticide is increased by adding cornstarch in a roach control measure was also established⁶⁾.

From the results obtained in the present tests, it is clear that corn meal, rice-bran and wheat bran are effective as baits for *Periplaneta americana* and *P. picea*, and sugar is enhanced the acceptability of these materials. While it

has been well known that these bait formulations are ineffective against *Blattella germanica*⁷⁾. In the present tests, effective materials in every time are sweetenings, while sugar and any material like sugar said to be not true attractants, but taste materials^{2, 3)}.

Résumé

In the present paper, the author dealt with the feeding preferences in two species of adult roaches, *Periplaneta americana* L. and *Periplaneta picea* Shiraki to various feeding-stuffs.

The roaches preferred some cereals such as corn meal, rice-bran and wheat bran, whereas they did not attracted for these materials when appreciable amount of flour or soybean was mixed with them.

Sugar, molasses or honey were suitable for their preferences, especially it was remarkable in *Periplaneta picea*.

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The Rate of Hydrolysis of Some Organophosphates. Chemical Studies on Organophosphorus Insecticides. IV. Rokurō SATŌ and Hiroshi KUBO (Agricultural Chemicals Inspection Station, Ministry of Agriculture and Forestry, Kodairamachi, Tokyo.) Received April 30, 1959. *Botyu-Kagaku*, 24, 89, 1959.

19. 有機燐剤のアルカリによる加水分解の反応速度論的考察 有機燐殺虫剤の化学的研究 第4報 佐藤六郎・久保博司(農林省農薬検査所) 34. 4. 30 受理

EP, MP 及び EPN のアルカリによる加水分解を反応速度論的に検討した。これらの三化合物はアルカリに対して本質的に EP>MP>EPN の順に安定であり P 原子の求電子的性質の弱い方が安定である。加水分解に際して反応系溶媒のメタノールと水との比率が増すにつれて加水分解速度が減少する。これは反応生成物 (*p*-nitrophenol-Na 塩) がアルコールよりも水に溶解し易い為と考えられる。ボルドー液中では EPN 乳剤の方が MP 乳剤よりも安定となるが、これは EPN の親油性に基くものと判断される。この際 Cu 成分は MP の加水分解を若干促進するが EPN に対しては特に影響を及ぼさない。

A kinetic study has been made of the hydrolysis of parathion, methyl parathion and EPN by alcoholic alkali or in Bordeaux mixture. The order of stability of these compounds in alkaline media can be arranged as follows; parathion > methyl parathion > EPN. In Bordeaux mixture EPN emulsion was found to be more stable than methyl parathion emulsion.

Recently many types of organophosphorus insecticides have gained considerable importance. Especially parathion, methyl parathion and EPN are very effectively used in Japan for the control of the rice stem borer and the various orchard pests. These compounds are closely related in their structure with *p*-nitrophenyl moiety. They differ, however, much in their stability against hydrolysis. Several investigations were done by Peck, D. ¹⁾; Ketelaar, J. ²⁾ and Heine, R. et al³⁾.

From the practical point of view mixed application of insecticides with fungicides is in general use to save troublesome operation of spraying chemicals and to obtain more effect against both insect and fungi. Particularly mixing organophosphates with Bordeaux mixture is practically prevailed, accordingly alkaline stability of organophosphates in Bordeaux mixture required to be clarified.

In this paper the kinetic investigation on parathion, methyl parathion and EPN are carried out in alcoholic media at 0°, 10° and 20° C (A) and in Bordeaux mixtures with different compositions at 0°, 20° and 30° C (B).

Materials and Methods

(A) In Alcoholic Medium

The compounds used were carefully refined and eliminated impurities. The reaction temperature was carefully controlled in a thermostat at 0°, 10° and 20° C.

The hydrolysis of all compounds was carried out in 0.01 N-sodium hydroxide, 0.01 M-sodium carbonate and 0.005 N-calcium hydroxide solution. The reaction was followed by measuring the liberation of *p*-nitrophenol colorimetrically at 400m μ in a Beckman DU type spectrophotometer.

(B) In Bordeaux Mixture

Two emulsifiable concentrates were prepared from refined compounds, *i. e.*

1) 40% methyl parathion in 25% toluene with 35% Sorpul 2020.

2) 45% EPN in 18% toluene with 37% Sorpul 2040.

Parathion was excluded from this experiment because it is fairly stable against Bordeaux mixture and offers practically no problem.

Three different kinds of Bordeaux mixtures were manufactured, *i. e.*

0.4–0.2%, 0.4–0.4% and 0.4–0.6% Bordeaux mixtures which were made by using 4g copper sulfate and 2g, 4g and 6g quicklime respectively to 1 litre water.

Additional Bordeaux mixtures which contain no copper sulfate were also made to clarify any effect of copper sulfate, *i. e.*

0–0.2%, 0–0.4% and 0–0.6% lime suspensions which were made by using 2g, 4g and 6g quicklime respectively to 1 litre water.

Definite amounts of emulsifiable concentrates were dropped in Erlenmeyer flasks and immersed in a water thermostat carefully controlled at 0° 20° and 30° C.

Freshly prepared Bordeaux mixtures kept in desired temperature were added into Erlenmeyer flasks to dilute 0.04% methyl parathion and 0.045% EPN emulsions respectively. The flasks were sealed with rubber plugs and shaken from time to time. At the definite time each 5ml of emulsions were pipetted out into 50ml volumetric flasks and added chilled methyl alcohol up to volume to make emulsion clear and filtrated as quickly as possible. The filtrates were quickly measured at 400m μ in 1cm cuvettes with a Beckman DU type spectrophotometer. The value of the absorption after completion of the reaction was also measured with each reaction flask.

Calculation

The hydrolysis of organophosphate esters in the alkaline solution is bimolecular process,

however, as the concentration of hydroxyl ions is much higher than that of the esters. Each reaction can be expected to the first order. The first order rate constant k defined as the equation.

$$k = \frac{2.303}{t} \log \frac{A_{\infty}}{A_{\infty} - A}$$

Where A is the corresponding absorbance at the arbitrary moment t and A_{∞} is the absorption after completion of hydrolysis. The true second order constant K (in $\text{mol}^{-1} \text{min}^{-1}$) can be calculated by dividing the apparent first order constant k by the concentration of the hydroxyl ions, expressed in mol/l .

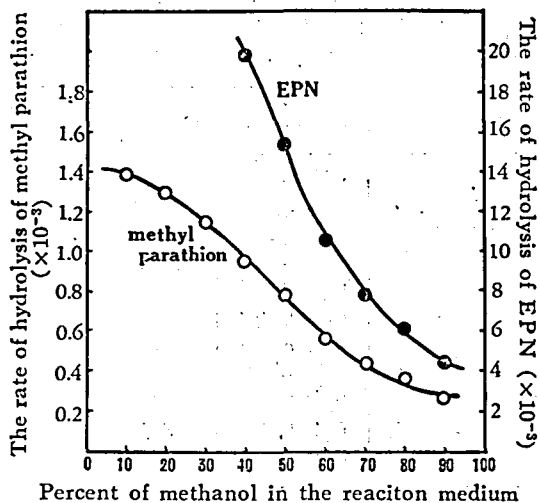
If we put $\log K$ versus $1/T$ we obtain the activation energy E and the logarithm of the frequency factor $\log n$.

$$\log K = \log n + \frac{E}{2.303 RT} \quad \text{where } R \text{ is gas constant.}$$

Results and Discussion

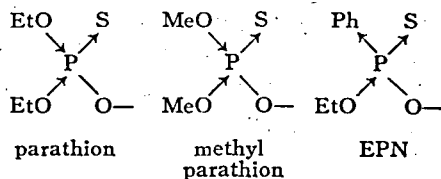
The rate constants K , activation energies E and frequency factors n for the hydrolysis in methanolic medium of organophosphates with alkali at 0° , 10° and 20°C are shown in Table 1.

In Fig. 1 the effect of solvent at 10°C is given. The change of solvent from less aqueous to a more aqueous medium accelerates the hydrolysis reaction. Methanol will decrease the thermodynamic probability of the reaction as the product (*p*-nitrophenol) is less solvated than water. Essential alkaline stability can be arranged as follows;



parathion > methyl parathion > EPN

This difference of alkaline stability can be explained from the basis of electrophilic character of phosphorus. Positive character of phosphorus can be weakened by electron release from the groups adjacent to phosphorus atom; i. e. Ethoxy groups release electron more easily than methoxy groups, on the other hand, phenyl group withdraws electron from phosphorus atom.



$K_{20} (\times 10^{-3})$ 0.19 0.71 10.8

Table 1. The kinetic data for the alkaline hydrolysis in 90% methanolic solution of organophosphate esters.

Compound	Alkali	log Frequency factor	Activation energy	Rate constant ($\times 10^{-3} \text{ mol}^{-1} \text{ sec}^{-1}$)		
				0	10	20°C
Parathion	NaOH	7.63	15300	0.025	0.077	0.19
	Na_2CO_3	7.61		0.022	0.065	0.17
	$\text{Ca}(\text{OH})_2$	7.34		0.025	0.089	0.22
Methyl parathion	NaOH	8.15	15200	0.095	0.253	0.71
	Na_2CO_3	8.07		0.080	0.216	0.63
	$\text{Ca}(\text{OH})_2$	7.72		0.071	0.214	0.59
E P N	NaOH	8.08	13500	1.88	4.42	10.78
	Na_2CO_3	7.99		1.49	3.82	9.34
	$\text{Ca}(\text{OH})_2$	7.73		1.64	3.78	8.64

Table 2. The kinetic data for the alkaline hydrolysis in Bordeaux mixtures of organophosphate esters.

Compound	Formula Bordeaux mixture	log Frequency factor	Activation energy	Rate constant ($\times 10^{-5} \text{ mol}^{-1} \text{ sec}^{-1}$)			pH
				0	20	30° C	
Methyl parathion	0.4-0.2%	6.96	15800	—	0.40	—	10.8
	0.4-0.4%			0.19	1.47	3.42	11.7
	0.4-0.6%			—	1.59	—	11.7
"	0 -0.2%	9.91		—	1.17	—	11.7
	0 -0.4%			0.17	1.24	3.10	11.7
	0 -0.6%			—	1.23	—	11.8
E P N	0.4-0.2%	3.43	11400	—	0.30	—	10.8
	0.4-0.4%			0.20	0.76	1.61	11.7
	0.4-0.6%			—	1.01	—	11.7
"	0 -0.2%	3.42		—	0.78	—	11.7
	0 -0.4%			0.19	0.76	1.54	11.7
	0 -0.6%			—	0.98	—	11.8

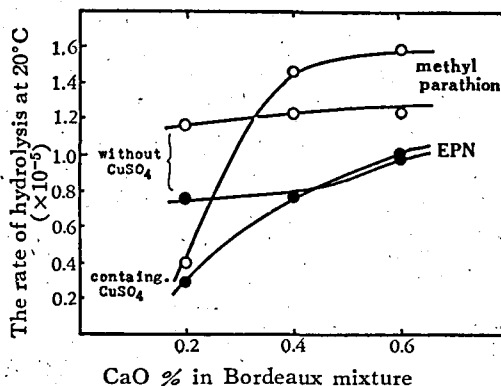
In case of Bordeaux mixture, the thermodynamic collision theory does not fit exactly on account of the heterogenous state of emulsion and the adsorption on the surface of $\text{CuSO}_4\text{-Ca(OH)}_2$ complex. The rate of hydrolysis showed some tendency to decrease gradually in the course of the long time. This tendency will be caused mainly by the cohesion of emulsion micelle and was more remarkable in EPN emulsion which has more lipophile property in itself. So kinetic investigations were carried out on emulsions before not so long time elapsed. In this case each reaction value was presented by the apparent first constant.

The rate constants K , activation energies E and frequency factors n for the hydrolysis of methyl parathion and EPN in Bordeaux mixture at 0°, 20° and 30° C are shown in Table 2.

EPN was more stable than methyl parathion in Bordeaux mixtures and its activation energy was somehow lower than that in methanolic media.

Some characteristic results of methyl parathion and EPN with different compositions of Bordeaux mixture are shown in Fig 2.

Although the percent of CaO was varied from 0.2 to 0.6 both the rate constant and pH of Bordeaux mixtures excepting CuSO_4 component showed very little differences. But in the



normal Bordeaux mixtures CuSO_4 brought some effects on the rate constant and pH *i. e.*

When CaO percent lessened, the alkalinity dropped down and the hydrolysis showed marked decrease. But when CaO was exceeded over 0.3% some kind of increment upon the hydrolysis occurred in the case of methyl parathion.

This fact seemed to have less connection with alkalinity but might be derived from some kind of activation on the surface of $\text{CuSO}_4\text{-Ca(OH)}_2$ complex.

But such activation could not be observed in the case of EPN.

Summary

The hydrolysis of parathion, methyl parathion

and EPN have been studied in alcoholic alkali media and in Bordeaux mixtures. In alcoholic media the order of instability of organophosphate esters against alkaline hydrolysis is in agreement with the order of electrophilic character of the phosphorus atom. The change of solvent from less to more aqueous medium accelerates the hydrolysis reaction. In Bordeaux mixtures EPN turns to stable considerably. Cupric component increases the hydrolysis of methyl parathion but EPN is not greatly affected by it.

Acknowledgments

We are most grateful to Mr. K. Ogawa for his technical assistance.

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The Chemical and Physical Properties of Talcs and their Behavior on the Decomposition of Methyl Parathion Dust Formulation. Chemical Studies on Organophosphorus Insecticides. V. Rokurō SATO and Hiroshi KUBO (Agricultural Chemicals Inspection Station, Ministry of Agriculture and Forestry, Kodairamachi, Tokyo) Received April 30, 1959. *Botyu-Kagaku* 24, 93, 1959.

20. タルクの物理化学的性質がメチルパラチオン粉剤の経時変化に及ぼす影響 有機磷殺虫剤の化学的研究 第5報 佐藤六郎・久保博司(農林省農薬検査所) 34. 4. 30 受理

メチルパラチオン粉剤の経時変化とその機構を明らかにする為、代表的 26 種の天然タルクの化学的・物理的性質、即ち水分吸着能 (I)、アンモニア吸着能 (II)、置換性カチオン (Mg, Ca, Al, Fe) (III)、塩基置換容量 (IV)、全塩基性 (V)、全酸度 (VI)、及び表面酸性 (VII) 等の特性を検討し、これらの性質とメチルパラチオンの分解との相関性を検討した。I, II, IV, V はメチルパラチオンの分解要因と深い関係を持つことが確認された。メチルパラチオンの分解機構はキャリアーの表面に分布した電気的陰性に基づく吸着活性点による求核的反応とその塩基性に基因するものと推測される。

This report presents the relationship between the chemical and physical properties of talcs and the rate of decomposition of the active ingredient of methyl parathion in dust formulation. Various factors of diluents having effect on the decomposition of methyl parathion were investigated. The amounts of moisture sorbed (I), that of ammonia chemisorbed (II), that of some replaceable cations, e. g. Mg, Ca, Fe and Al (III), the base exchange capacity (IV), total basicity (V), total acidity (VI) and surface acidity (VII) have been measured on the various talcs commercially available for the dust formulation. The considerably high relationships were obtained between the data of I, II, IV and V and the rate of decomposition of methyl parathion. The results are consistent with the proposal that the reaction involves a nucleophilic attack to the phosphorous atom of methyl parathion molecule by the negatively charged points distributed over the active surface of talcs.

Introduction

In contrast to the extensive literatures dealing with the organophosphorus insecticides, very little is known yet concerning the behavior of carriers or diluents on the active

ingredient in dust formulation.^{1,2,3} During long storage severe decomposition of the active ingredient in some organophosphorus insecticides have been taken place actually. Especially the loss of the active ingredient in methyl parathion dust has become an serious industrial